



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number: **0 664 332 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **94870007.5**

(51) Int. Cl.⁸: **C11D 3/00, C11D 3/37**

(22) Date of filing: **19.01.94**

(43) Date of publication of application:
26.07.95 Bulletin 95/30

(84) Designated Contracting States:
**AT BE CH DE DK ES FR GB GR IE IT LI LU NL
PT SE**

(71) Applicant: **THE PROCTER & GAMBLE
COMPANY**
One Procter & Gamble Plaza
Cincinnati,
Ohio 45202 (US)

(72) Inventor: **Fredj, Abdennaceur**
Avenue des croix de guerre 191
B-1120 Brussel (BE)
Inventor: **Willey, Alan David**
7 Brandon Grove,
Sandyford
Newcastle upon Tyne NE2 1PA (GB)

Inventor: **Toen, Christiaan Arthur Jacques**
Kamiel

Boekwelthofstraat 4
B-9120 Haasdonk (BE)

Inventor: **Hardy, Frederick Edward**
8 Woodend,
Darras Hall

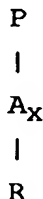
Ponteland,
Newcastle upon Tyne NE20 (GB)

Inventor: **Johnston, James Pyott**
Weidelaan 17
B-3090 Overijse (BE)

(74) Representative: **Canonici, Jean-Jacques et al**
Procter & Gamble European Technical
Center N.V.
Temselaan 100
B-1853 Strombeek-Bever (BE)

(54) **Detergent compositions inhibiting dye transfer.**

(57) **A dye transfer inhibiting composition comprising a mixture of polyamine N-oxide polymers having a low and high oxidation degree, said polyamine N-oxide polymers containing units having the following structure formula :**

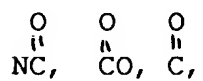


wherein

P is a polymerisable unit, whereto the N-O group can be attached to or wherein the N-O group forms part of the polymerisable unit.

A is

EP 0 664 332 A1



-O-, -S-,



x is O or 1;

R are aliphatic, ethoxylated aliphatic, aromatic, heterocyclic or alicyclic groups where the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

Field of the Invention

The present invention relates to a composition and a process for inhibiting dye transfer between fabrics during washing. More in particular, the present invention relates to dye transfer inhibiting compositions comprising a mixture of polyamine N-oxide polymers having a low oxidation degree and polyamine N-oxide polymers having a high oxidation degree.

Background of the Invention

One of the most persistent and troublesome problems arising during modern fabric laundering operations is the tendency of some colored fabrics to release dye into the laundering solutions. The dye is then transferred onto other fabrics being washed therewith.

One way of overcoming this problem would be to complex or adsorb the fugitive dyes washed out of dyed fabrics before they have the opportunity to become attached to other articles in the wash.

Polymers have been used within detergent compositions to inhibit dye transfer. EP-A-O 102 923 describes the use of carboxyl containing polymers within aqueous compositions. DE-A-2 814 329 discloses the use of N-vinyl-oxazolidone polymers and FR-A-2 144 721 discloses the use of 15-35% of a copolymer of polyvinylpyrrolidone and acrylic acid nitrile or maleic anhydride within a washing powder.

EP-265 257 describes detergent compositions comprising an alkali-metal carboxy-metal carboxymethyl-cellulose, a vinylpyrrolidone polymer and a polycarboxylate polymer.

It has now been surprisingly found that a particular combination of polyamine N-oxide polymers having a low oxidation degree and polyamine N-oxide polymers having a high oxidation degree are very efficient in eliminating transfer of a broad range of solubilized or suspended dyes. This finding allows to formulate compositions which exhibit excellent dye transfer inhibiting properties over a broad selection of dyes.

According to another embodiment of this invention a process is also provided for laundering operations involving colored fabrics.

Summary of the Invention

The present invention relates to inhibiting dye transfer compositions comprising a mixture of polyamine N-oxide polymers having a low oxidation degree and polyamine N-oxide polymers having a high oxidation degree.

Detailed description of the invention

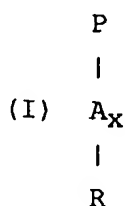
The compositions of the present invention comprise a mixture of polyamine N-oxide polymers having a low oxidation degree ("LOPAO") and polyamine N-oxide polymers having a high oxidation degree ("HOPAO").

By "polyamine N-oxide polymers having a low oxidation degree" as used herein, is meant polyamine N-oxide polymers wherein the ratio of amine to amine N-oxide is from 1000:1 to 1:1, more preferably from 100:1 to 1:1, most preferably from 10:1 to 1:1.

By "polyamine N-oxide polymers having a high oxidation degree" as used herein, is meant polyamine N-oxide polymers wherein the ratio of amine to amine N-oxide is from 2:3 to 1:1000000, more preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000.

The amount of amine oxide groups present in said polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation.

The polyamine N-oxide polymers contain units having the following structure formula :

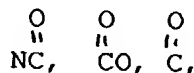


wherein

P is a polymerisable unit, whereto the N-O group can be attached to or wherein the N-O group forms part of the polymerisable unit or a combination of both.

A is

5



10

-O-, -S-,

15

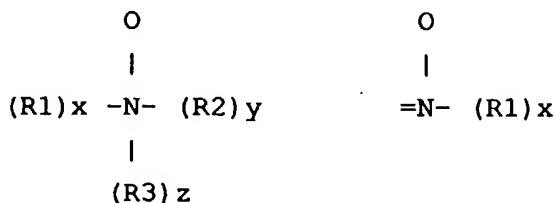


x is 0 or 1;

20 R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures:

25



30

35 wherein

R1, R2, R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit. Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups.

Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

- The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a $\text{PKa} < 10$, preferably $\text{PKa} < 7$, more preferred $\text{PKa} < 6$.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

- Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

The polyamine N-oxides of the present invention are typically present from 0.001 to 10% , more preferably from 0.01 to 2%, most preferred from 0.05 to 1% by weight of the dye transfer inhibiting composition.

- The present compositions are conveniently used as additives to conventional detergent compositions for use in laundry operations. The present invention also encompasses dye transfer inhibiting compositions which will contain detergent ingredients and thus serve as detergent compositions.

Methods for making polyamine N-oxides :

The production of the polyamine-N-oxides may be accomplished by polymerizing the amine monomer and oxidizing the resultant polymer with a suitable oxidizing agent, or the amine oxide monomer may itself be polymerized to obtain the polyamine N-oxide.

- The synthesis of polyamine N-oxide can be exemplified by the synthesis of polyvinyl-pyridine N-oxide. Poly-4-vinylpyridine ex Polysciences (mw. 50 000, 5.0 g., 0.0475 mole) was predissolved in 50 ml acetic acid and treated with a peracetic acid solution (25 g of glacial acetic acid, 6.4 g of a 30% vol. solution of H_2O_2 , and a few drops of H_2SO_4 give 0.0523 mols of peracetic acid) via a pipette. The mixture was stirred over 30 minutes at ambient temperature (32 C). The mixture was then heated to 80-85 C using an oil bath for 3 hours before allowing to stand overnight. The polymer solution then obtained is mixed with 1l of acetone under agitation. The resulting yellow brown viscous syrup formed on the bottom is washed again with 1l of acetone to yield a pale crystalline solid.

The solid was filtered off by gravity, washed with acetone and then dried over P_2O_5 .

The amine : amine N-oxide ratio of this polymer is 1:4.

DETERGENT ADJUNCTS

A wide range of surfactants can be used in the detergent compositions. A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in US Patent 3,664,961 issued to Norris on May 23, 1972.

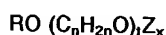
- Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulphonate and sulphate surfactants in a weight ratio of from 5:1 to 1:2, preferably from 3:1 to 2:3, more preferably from 3:1 to 1:1. Preferred sulphonates include alkyl benzene sulphonates having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid esters in which the fatty acid is derived from a C_{12} - C_{18} fatty source preferably from a C_{16} - C_{18} fatty source. In each instance the cation is an alkali metal, preferably sodium. Preferred sulphate surfactants are alkyl sulphates having from 12 to 18 carbon atoms in the alkyl radical, optionally in admixture with ethoxy sulphates having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6. Examples of preferred alkyl sulphates herein are tallow alkyl sulphate, coconut alkyl sulphate, and C_{14} - C_{15} alkyl sulphates. The cation in each instance is again an alkali metal cation, preferably sodium.

- One class of nonionic surfactants useful in the present invention are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 13.5, more preferably from 10 to 12.5. The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Especially preferred nonionic surfactants of this type are the C_9 - C_{15} primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C_{14} - C_{15} primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol and the C_{12} - C_{14} primary alcohols containing 3-5

moles of ethylene oxide per mole of alcohol.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula

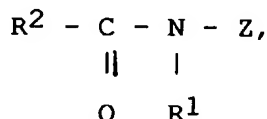


5

wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent are disclosed in EP-B 0 070 077, 0 075 996 and 0 094 118.

10

Also suitable as nonionic surfactants are poly hydroxy fatty acid amide surfactants of the formula



15

wherein R¹ is H, or R¹ is C₁₋₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R² is C₅₋₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R¹ is methyl, R² is a straight C₁₁₋₁₅ alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B or HS. Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate (Na₂Si₂O₅).

Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethylloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -hexacarboxylates and and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the present compositions include a mixture of a water-insoluble

aluminosilicate builder such as zeolite A or of a layered silicate (sks/6), and a water-soluble carboxylate chelating agent such as citric acid.

A suitable chelant for inclusion in the detergent compositions in accordance with the invention is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt thereof. Examples of such preferred sodium salts of EDDS include Na₂EDDS and Na₄EDDS. Examples of such preferred magnesium salts of EDDS include MgEDDS and Mg₂EDDS. The magnesium salts are the most preferred for inclusion in compositions in accordance with the invention.

Especially for the liquid execution herein, suitable fatty acid builders for use herein are saturated or unsaturated C10-18 fatty acids, as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid.

Preferred builder systems for use in granular compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid.

Other builder materials that can form part of the builder system for use in granular compositions the purposes of the invention include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 10% to 80% by weight of the composition preferably from 20% to 70% and most usually from 30% to 60% by weight.

Detergent ingredients that can be included in the detergent compositions of the present invention include bleaching agents. These bleaching agent components can include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present bleaching compounds will typically be present at levels of from about 1% to about 10%, of the detergent composition. In general, bleaching compounds are optional components in non-liquid formulations, e.g. granular detergents. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition.

The bleaching agent component for use herein can be any of the bleaching agents useful for detergent compositions including oxygen bleaches as well as others known in the art.

In a method aspect, this invention further provides a method for cleaning fabrics, fibers, textiles, at temperatures below about 50 °C especially below about 40 °C, with a detergent composition containing polyamine N-oxide containing polymers, optional auxiliary detergent surfactants, optional detergent adjunct ingredients, and a bleaching agent.

The bleaching agent suitable for the present invention can be an activated or non-activated bleaching agent.

One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxydecanoic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

Preferably, the bleaches suitable for the present invention include peroxygen bleaches. Examples of suitable water-soluble solid peroxygen bleaches include hydrogen peroxide releasing agents such as hydrogen peroxide, perborates, e.g. perborate monohydrate, perborate tetrahydrate, persulfates, percarbonates, peroxydisulfates, perphosphates and peroxyhydrates. Preferred bleaches are percarbonates and perborates.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetylenediamine(TAED), nonanoyloxybenzenesulfonate (NOBS, described in US 4,412,934), 3,5-trimethylhexanoyloxybenzenesulfonate (ISONOBS, described in EP 120,591) or pentaacetylglucose (PAG),

which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Also suitable activators are acylated citrate esters (ATC) such as disclosed in Copending European Patent Application No. 91870207.7.

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Other peroxygen bleaches suitable for the present invention include organic peroxyacids such as percarboxylic acids.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

Other detergent ingredients that can be included are deterative enzymes which can be included in the detergent formulations for a wide variety of purposes including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and prevention of refugee dye transfer. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.05 mg to about 3 mg, of active enzyme per gram of the composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames Alcalase, Savinase and Esperase by Novo Industries A/S (Denmark) and Maxatase by International Bio-Synthetics, Inc. (The Netherlands) and FN-base by Genencor, Optimase and opticlean by MKC.

Of interest in the category of proteolytic enzymes, especially for liquid detergent compositions, are enzymes referred to herein as Protease A and Protease B. Protease A is described in European Patent Application 130,756. Protease B is described in European Patent Application Serial No. 87303761.8. Amylases include, for example, -amylases obtained from a special strain of *B. licheniformis*, described in more detail in British Patent Specification No. 1,296,839 (Novo). Amylolytic proteins include, for example, Rapidase, Maxamyl (International Bio-Synthetics, Inc.) and Termamyl (Novo Industries).

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2,075,028; GB-A-2,095,275 and DE-OS-2,247,832.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800, and cellulases produced by a fungus of *Bacillus* N or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusc (*Dolabella Auricula* Solander).

Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Such cellulase are described in Copending European patent application No. 93200811.3, filed March 19, 1993.

Especially suitable cellulase are the cellulase having color care benefits. Examples of such cellulases are cellulase described in European patent application No. 91202879.2, filed November 6, 1991 Carezyme (Novo).

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19,154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P".

Especially suitable Lipase are lipase such as M1 Lipase (Ibis) and Lipolase (Novo).

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes of pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991.

In liquid formulations, an enzyme stabilization system is preferably utilized. Enzyme stabilization techniques for aqueous detergent compositions are well known in the art. For example, one technique for enzyme stabilization in aqueous solutions involves the use of free calcium ions from sources such as calcium acetate, calcium formate and calcium propionate. Calcium ions can be used in combination with short chain carboxylic acid salts, preferably formates. See, for example, U.S. patent 4,318,818. It has also been proposed to use polyols like glycerol and sorbitol. Alkoxy-alcohols, dialkylglycoethers, mixtures of polyvalent alcohols with polyfunctional aliphatic amines (e.g., such as diethanolamine, triethanolamine, diisopropanolamine, etc.), and boric acid or alkali metal borate. Enzyme stabilization techniques are additionally disclosed and exemplified in U.S. patent 4,261,868, U.S. Patent 3,600,319, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5. Non-boric acid and borate stabilizers are preferred. Enzyme stabilization systems are also described, for example, in U.S. Patents 4,261,868, 3,600,319 and 3,519,570.

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application N 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

Especially preferred detergent ingredients are combinations with technologies which also provide a type of color care benefit. Examples of these technologies are cellulase and/or peroxidases and/or metallo catalysts for color maintenance rejuvenation.

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alcanols. Suitable 2-alkyl-alcanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N° 92201649.8.

Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil®.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

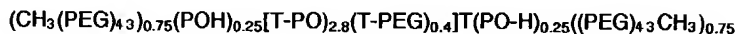
Other components used in detergent compositions may be employed, such as soil-suspending agents soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and non-encapsulated and encapsulated perfumes.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino-s-triazin-6-ylamino)stilbene-2,2'-disulphonate, disodium 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostilbene-2,2'-disulphonate, disodium 4,4'-bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2,2'-disulphonate, monosodium 4',4''-bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2-sulphonate, disodium 4,4'-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'-disulphonate, disodium 4,4'-bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2'-disulphonate, disodium 4,4'-bis-(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'-disulphonate and sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3-triazole-2''-sulphonate.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula



where PEG is $-(\text{OC}_2\text{H}_4)_n\text{O}-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pCOC}_6\text{H}_4\text{CO})$.

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propanediol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane-1,2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfofenzoid acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3,000. The polyesters and their method of preparation are described in detail in EPA 311 342.

The detergent compositions according to the invention can be in liquid, paste, gels or granular forms. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l; in such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt. The liquid compositions according to the present invention can also be in "concentrated form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents. Typically, the water content of the concentrated liquid detergent is less than 30%, more preferably less than 20%, most preferably less than 10% by weight of the detergent compositions.

The present invention also relates to a process for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

The process comprises contacting fabrics with a laundering solution as hereinbefore described.

The process of the invention is conveniently carried out in the course of the washing process. The washing process is preferably carried out at 5 °C to 75 °C, especially 20 to 60, but the polymers are effective at up to 95 °C and higher temperatures. The pH of the treatment solution is preferably from 7 to 11, especially from 7.5 to 10.5.

The process and compositions of the invention can also be used as detergent additive products.

Such additive products are intended to supplement or boost the performance of conventional detergent compositions.

The detergent compositions according to the present invention include compositions which are to be used for cleaning substrates, such as fabrics, fibers, hard surfaces, skin etc., for example hard surface cleaning compositions (with or without abrasives), laundry detergent compositions, automatic and non automatic

dishwashing compositions.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention, said scope being determined according to claims which follow.

- 5 A liquid detergent composition according to the present invention is prepared, having the following compositions :

Table I

10

15

20

% by weight of the total detergent composition	
Linear alkylbenzene sulfonate	10
Alkyl sulphate	4
Fatty alcohol (C ₁₂ -C ₁₅) ethoxylate	12
Fatty acid	10
Oleic acid	4
Citric acid	1
NaOH	3.4
Propanediol	1.5
Ethanol	10

25

The extent of dye transfer is assessed by a Hunter Colour measurement. The Hunter Colour system evaluates the colour of a fabric sample in terms of the Dc value which represents the change in the Hunter *a*, *b* values which are determined by reflecting spectofotometry. The Dc value is defined by the following equation:

$$Dc = \{(a_i - a_f)^2 + (b_i - b_f)^2\}^{1/2}$$

30

where the subscripts *i* and *f* refer to the Hunter value before and after washing in the presence of the bleeding fabric, respectively. The least significant difference is 1 at 95% confidence level.

EXAMPLE I

35

The extent of dye transfer from different colored fabrics was studied using a launder-o-meter test that simulates a 30 min wash cycle. The launder-o-meter beaker contains 200 ml of a detergent solution, a 10cmx10cm piece of the colored fabric and a multifiber swatch which is used as a pick-up tracer for the bleeding dye. The bleeding dye consists of one part direct blue 90, one part direct blue 112 and one part direct violet 47. The multifiber swatch consists of cotton.

40

Experimental conditions:

pH = 7.8

45

A: A detergent composition according to Table I which does not contain any dye transfer inhibition system.

B: A detergent composition according to Table I containing 10 ppm of PVNO (poly(4-vinylpyridine-N-oxide)) which has an average molecular weight of about 10,000 and an amine to amine N-oxide ratio of 1:10 (HOPAO)

50

C: A detergent composition according to Table I containing 10 ppm of PVNO (poly(4-vinylpyridine-N-oxide)) which has an average molecular weight of about 30,000 and an amine to amine N-oxide ratio of 1:1 (LOPAO).

D: A detergent composition according to Table I containing 5ppm of PVNO (poly(4-vinylpyridine-N-oxide)) which has an average molecular weight of about 30,000 and an amine to amine N-oxide ratio of 1:10, and 5ppm of PVNO (poly(4-vinylpyridine-N-oxide)) which has an average molecular weight of about 30,000 and an amine to amine N-oxide ratio of 1:1 (HOPAO + LOPAO).

55

Results: Dc values for the cotton pick-up tracer.

Bleeding fabric color	A	B	C	D
Direct Blue 90/Direct Blue 112 and Direct Violet 47	10.3	4.2	4.5	3

EXAMPLE II (A/B/C/D)

Liquid detergent compositions according to the present invention are prepared, having the following compositions :

		<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
15	Linear alkylbenzene sulfonate	18	-	6	-
	C ₁₂ -C ₁₅ alkyl sulfate	-	16.0	-	-
	C ₁₂ -C ₁₅ alkyl ethoxylated sulfate	-	11.0	4.0	25.0
	C ₁₂ -C ₁₄ N-methyl glucamide	-	7.0	9.0	9.0
	C ₁₂ -C ₁₄ fatty alcohol ethoxylate	12.0	5.0	6.0	6.0
20	C ₁₂ -C ₁₆ fatty acid	9.0	6.8	14.0	14.0
	Fatty acid	10	10	10	10
	Oleic acid	4	4	4	4
	Citric acid	1	1	1	1
	Diethylenetriaminepentamethylene phosphonic acid	1.5	1.5	1.5	1.5
25	Propanediol	1.5	1.5	1.5	1.5
	Ethanol	10	10	10	10
	Ethoxylated tetraethylene pentamine	0.7	0.7	0.7	0.7
	Poly(4-vinylpyridine)-N-oxide (HOPAO)	0.3	0.3	0.3	0.3
	Poly(4-vinylpyridine)-N-oxide (LOPAO)	0.3	0.3	0.3	0.3
30	Thermamyl	0.13	0.13	0.13	0.13
	Carezyme	0.014	0.014	0.014	0.014
	FN-Base	1.8	1.8	1.8	1.8
	Lipolase	0.14	0.14	0.14	0.1
	Endoglucanase A	0.53	0.53	0.53	0.53
35	Suds supressor (ISO FOL')	2.5	2.5	2.5	2.5
	Water and Minors	up to 100			
NaOH and/or MEA to adjust pH to 7.8					

EXAMPLE III (A/B/C/D)

Compact granular detergent compositions according to the present invention are prepared, having the following formulation:

% by weight of the total detergent composition				
	A	B	C	D
5	Polyhydroxy fatty acid amide	10	-	-
	Alkyl alkoxylated sulfate	-	9	9
	Alkyl sulphate	4.80	4.80	4.80
	C ₁₄₋₁₅ alcohol 7 times ethoxylate	4.00	4.00	4.00
	Tallow alcohol 11 times ethoxylated	1.8	1.80	1.8
10	Dispersant	0.07	0.07	0.07
	Silicone fluid	0.80	0.80	0.80
	Trisodium citrate	14.00	14.00	14.00
	Citric acid	3.00	3.00	3.00
	Zeolite	25.00	20.00	32.50
15	Diethylenetriamine pentamethylene phosphonic acid	0.6	0.6	0.6
	Maleic acid acrylic acid copolymer	5.00	5.00	5.00
	Carezyme T-granulate	0.2	0.5	0.3
	Alcalase T-granulate	0.60	0.60	0.20
	Lipolase T-granulate	0.20	0.10	0.25
20	Termamyl T-granulate	0.3	0.3	0.3
	Sodium silicate	2.00	2.00	2.00
	Sodium sulphate	3.50	3.50	3.50
	Percarbonate	-	-	20
	Perborate	15	15	-
25	TAED	-	5	-
	Encapsulated perfume	0.2	-	-
	Perfume	0.3	0.2	0.3
	Poly(4-vinylpyrrolidone) N-oxide (HOPAO)	0.3	0.3	0.3
	Poly(4-vinylpyrrolidone) N-oxide (LOPAO)	0.3	0.3	0.3
30	Minors	up to 100		

Claims

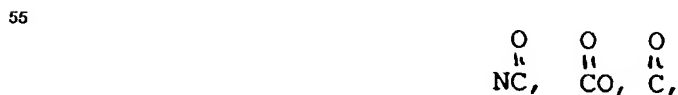
- 35 1. A dye transfer inhibiting composition comprising a mixture of polyamine N-oxide polymers having a low and high oxidation degree, said polyamine N-oxide polymers containing units having the following structure formula :



wherein

50 P is a polymerisable unit, where to the N-O group can be attached to or wherein the N-O group forms part of the polymerisable unit.

A is



-O-,S-,



5

x is 0 or 1;

R are aliphatic, ethoxylated aliphatic, aromatic, heterocyclic or alicyclic groups whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

10

2. A dye transfer inhibiting composition according to claim 1 wherein P is a polymerisable unit wherein the N-O group is attached to and wherein R is selected from an aromatic or heterocyclic group.
3. A dye transfer inhibiting composition according to claim 2 wherein the nitrogen of the N-O group forms part of the R-group.
4. A dye transfer inhibiting composition according to claim 3 wherein the R-group is selected from pyridine, pyrrole, quinoline, acridine, imidazole and derivatives thereof.
5. A dye transfer inhibiting composition according to claim 1,2 wherein the nitrogen of the N-O group is attached to the R-group.
6. A dye transfer inhibiting composition according to claim 5 wherein R is a phenyl group.
7. A dye transfer composition according to claim 1 wherein P is a polymerisable unit, whereto the N-O group forms part of the polymerisable unit and wherein R is selected from an aromatic or heterocyclic group.
8. A dye transfer inhibiting composition according to claim 7 wherein the nitrogen of the N-O group forms part of the R-group.
9. A dye transfer inhibiting composition according to claim 8 wherein the R-group is selected from pyridine, pyrrole, quinoline, acridine, imidazole and derivatives thereof.
10. A dye transfer inhibiting composition according to claim 1-9 wherein the polymeric backbone is derived from the group of the polyvinyl polymers.
11. A dye transfer inhibiting composition according to claim 1-10 wherein said polyamine N-oxide polymers having a low oxidation degree has a ratio of amine to amine N-oxide from 1000:1 to 1:1, preferably from 100:1 to 1:1, most preferably from 10:1 to 1:1 and wherein said polyamine N-oxide polymer having a low oxidation degree has a ratio of amine to amine N-oxide from 2:3 to 1:1000000, preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000.
12. A dye transfer inhibiting composition according to claims 1-11 wherein the polyamine N-oxide has an average molecular weight within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.
13. A dye transfer inhibiting composition according to claims 1-12 wherein the polyamine N-oxide is present at levels from 0.001 to 10 % by weight of the composition.
14. A dye transfer inhibiting composition according to claim 1-13 which is a detergent additive, in the form of a non-dusting granule or a liquid.
15. A detergent composition which comprises a dye transfer inhibiting composition according to claims 1-14 further comprising surfactants, builders, enzymes and other conventional detergent ingredients.

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 87 0007

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P, X	EP-A-0 579 295 (THE PROCTER & GAMBLE COMPANY) * the whole document * ---	1-10, 12-15	C11D3/00 C11D3/37
A	EP-A-0 135 217 (THE PROCTER & GAMBLE COMPANY) * page 5, line 35 - page 7, line 30 * * page 13, line 25 - page 16, line 22 * * page 34, line 30 - page 35, line 16 * * page 47, line 13 - page 48, line 4 * -----	1, 10, 13-15	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 June 1994	Examiner Doolan, G
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document	